

ADSORPTION OF Cu^{2+} , As^{3+} AND Cd^{2+} IONS FROM AQUEOUS SOLUTION BY EGGSHELL

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ABSTRACT

The adsorption of Cu^{2+} , Cd^{2+} and As^{3+} ions on eggshell from aqueous solution was studied under batch conditions at 30, 40, 50 and 60°C and concentrations of 10, 20, 30, 60 and 80 mg/l. The partition coefficient for the ions between aqueous solution and chicken eggshell increased with time and with increase in the concentration of metal ions in solution, but decreased with increase in temperature which is suggestive of physical adsorption on the eggshell. Activation energies of 8.50, 9.25 and 11.74 kJmol^{-1} were obtained for the adsorption of Cu^{2+} , As^{3+} and Cd^{2+} respectively which also suggest physical adsorption. Sorption of As^{3+} and Cd^{2+} from solution onto the eggshell adsorbent was found to follow pseudo-first order mechanism while that of Cu^{2+} was found to follow the pseudo-second order mechanism. Experimental data obtained for the adsorption of the metal ions by eggshell fit the Freundlich adsorption isotherm.

KEY WORDS: Adsorption; Aqueous Solution; Heavy Metals; Partition Coefficient

INTRODUCTION

Contamination from the increasing technological development and industrialization has been known to disrupt and destroy the fragile ecology through indiscriminate discharge of industrial and municipal wastes into the sea. The pollution of the marine environment by petroleum and chemical spillage and sewage disposal has led to the focus of the world on the need for the controlled use of resources and the planned disposal of waste products.

According to Kobya *et al.* (2005), heavy metals are metallic chemical elements with relatively high densities which are toxic or poisonous even at low concentrations. It is well recognized that the presence of heavy metals in the environment has resulted in a number of environmental problems, the greatest of which is water pollution (Padmavathy *et al.*, 2003). According to Okuo and Ozioko (2001), wastes from industries constitute 62 % of the total source of heavy metal pollutants in rivers and other water bodies around us. In recent years, management of pollution caused by heavy metals has been a major problem, especially in developing countries. These heavy metals are introduced into the environment through industrial activities such as agro-based, pharmaceutical, oil and steel-based industries. They are known to progressively accumulate in our ecosystem once they are introduced, from very low levels to levels that exceed the threshold in the environment. Most of these metals such as cadmium, lead, arsenic, mercury, chromium, cobalt and nickel are very toxic. They are carcinogenic and at very

high concentrations, may lead to brain damage (Yoo *et al.*, 2002).

Unlike organic pollutants, heavy metals do not biodegrade, and thus, pose a different kind of challenge for remediation. In order to remove toxic heavy metals from water bodies, several methods have been suggested and investigated. Although chemical precipitation, coagulation, ion-exchange, solvent extraction, filtration, evaporation and membrane methods have been applied for this purpose, most of these techniques have some limitations such as requirement of several pretreatments and additional treatments. In addition, some of them are less effective and require high capital cost (Volesky, 1990; Kam *et al.*, 2002; Kim, 2002).

It was only in the 1990s that a new scientific area, biosorption was developed that could help in the recovery of heavy metals. Metal-sequestering properties of non-viable microbial biomass provide a basis for a new approach to the removal of heavy metals when they occur at low concentrations (Volesky, 1990). Therefore, many researchers have applied regenerated wastes to treat heavy metals from aqueous solutions (Dipak *et al.*, 1993; Cho, 1994; Lee, 1994; Chiron *et al.*, 2003).

This study was carried out using chicken eggshell powder as the adsorbent for the removal of cadmium, copper and arsenic from wastewater. About 95 % of the dry eggshell is CaCO_3 weighing 5.5 g from the weight of an eggshell which is approximately 5.80 g and contains about 0.3 % P, 0.3 % Mg and traces of Na, K, Zn, Fe and Cu.

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MATERIALS AND METHODS

2.1 Materials

Chicken eggshells were collected from Adrian’s Bakery, Calabar, Cross River State. To remove impurities and interference materials, the samples were rinsed several times with tap water and de-ionized water (Park *et.al.*, 2007). It was then dried in an oven for 12 hours at 100°C, ground to powder and preserved in a clean air-tight glass container.

All reagents used for this study were of analytical reagent grade and were procured from Globus Chemicals, Calabar. 100mg/l aqueous solution of the metal ions was prepared as stock from their salts (CuSO₄, As₂O₃, and CdSO₄). From the stock, working solutions of 10, 20, 30, 60 and 80mg/l were prepared

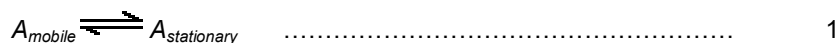
from appropriate aliquots diluted to the appropriate concentrations.

2.2 Methods

Adsorption experiments were carried out using batch mode at varied temperatures. 0.5g of the adsorbent was mixed with 25ml of each metal ion solution of known initial concentrations and the system kept in agitation using a rotary shaker for time intervals of 30, 60, 90, 120, 150 and 180 mins. At the end of each experiment, the content of each tube was filtered and the concentration of residual metal ions in each filtrate was determined using a UV Spectrophotometer (Hach DR/3000 model). The sorption of metal ions onto the eggshell powder was examined using agitation times of 30 – 180mins, initial metal ion concentrations of 10, 20, 30, 60 and 80 mg/l and temperatures of 30°C – 60°C.

RESULTS AND DISCUSSION

The distribution of an analyte between phases can often be described quite simply. An analyte is in equilibrium between the two phases;



Partition coefficient, K_D , is defined as the ratio of concentration, C , of a dissolved test substance in a two-phase system consisting of a sorbent (stationary phase) and an aqueous (mobile) phase i.e.

$$K_D = \frac{C_s}{C_m} \dots\dots\dots 2$$

where C_s is the concentration of metal ion in the solid phase (eggshell surface) and C_m is the concentration in the aqueous phase.

3.1 Effect of contact time

Table 1 shows the variation of the concentration of metal ions in solution after sorption and concentration of ions adsorbed with time at 30°C. It is observed that the concentration of metal ions adsorbed on the eggshell surface increased with time. This is due to the migration of higher fraction of the metal ions from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent as time progresses (Okuo and Ozioko 2001). This enhanced sorption of the metal ion with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in kinetic energy of the hydrated metal ions (Okuo and Ozioko 2001).

The rate of removal of the three metal ions was quite rapid initially, but gradually became slower with time until the maximum time of 180 minutes as depicted in figure 1. The initial faster rate may be due to the availability of the uncovered surface area of the adsorbent, since adsorption rate depends on the surface area of the adsorbent (Park *et al.*, 2007). The ground form of the adsorbent provides a wider surface area for the adsorption process. In addition, the adsorptive ability of eggshell may be attributed to the nature and concentration of its surface functional groups (active sites) which are responsible for interaction with the metal ions. Eggshell contains abundant cellulosic units including carbonate functional group (CO₃²⁻) containing oxygen atoms which probably serve as the active sites on which the metal ions are adsorbed on the eggshell.

The oxygen atoms in the eggshell molecule (CaCO₃) are sites with comparatively high reactivity (than the carbon atom) and hence have higher attraction for electrons.

Increase in the concentration of metal ions adsorbed with time results in a corresponding increase in the partition coefficient of each metal ion with time as depicted in figure 2.

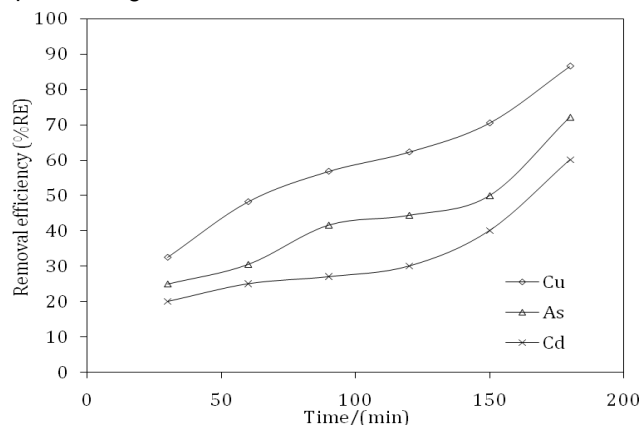


FIG.1: Variation of removal efficiency for metal ions with time.

3.2 Effect of metal ion concentration

Variation of initial concentration of metal ions in solution at 30°C resulted in an increase in the concentration adsorbed on the eggshell as shown in Table 2. This is due to the fact that as the concentration is increased, more metal ions are available in the solution for the adsorption process. Consequently, the partition coefficient of each metal ion increases as its

initial concentration in the aqueous phase increases as shown in figure 3.

Variations in the concentration of each metal ion adsorbed at time *t* and concentration *c_i* may be attributed to the differences in the sizes of the metal ions. Experimental data have shown that the size of heavy metal ions plays a role in the relative uptake of the metal ions in solution (Okiemen *et al.*, 1991). The

Table 1: Concentration of metal ions in solution after sorption (c_t) and concentration of metals adsorbed at various time intervals (Y_t) at 30°C

Time interval, <i>t</i> (mins)	c _t (mg/l)			Y _t (mg/l)		
	Cu ²⁺	Cd ²⁺	As ³⁺	Cu ²⁺	Cd ²⁺	As ³⁺
0	10.00	10.00	10.00	-	-	-
30	6.75	8.00	7.50	3.25	2.00	2.50
60	5.18	7.50	6.94	4.82	2.50	3.06
90	4.32	7.30	5.83	5.68	2.70	4.17
120	3.77	7.00	5.56	6.23	3.00	4.44
150	2.95	6.00	5.00	7.05	4.00	5.00
180	1.35	4.00	2.78	8.65	6.00	7.22

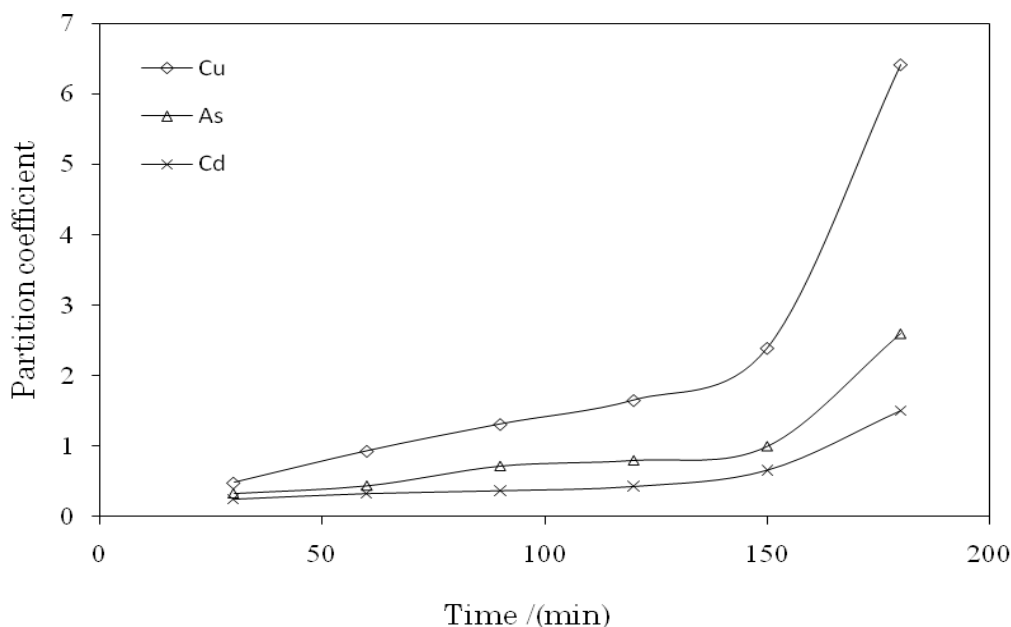


FIG. 2: Variation of partition coefficient of metal ions with time.

general pattern of uptake of metal ions shows that the larger the size of the metal ions, the greater their degree of uptake. This may be due to the fact that metal ions form aquo complexes in solution (Cotton and Wilkinson, 1972). The relative uptake of the different metal ions may therefore be said to be inversely proportional to their hydration energies, which of course has an inverse proportionality with metal ion size. Because the displacement of water molecules from the aquo ion is the nexus in adsorption dynamics, the stability of the aquo ion comes into play. The aquo ion stability can be estimated from the hydration energy of the metal ion and

is found to be dependent on the size of the ion. Hence, the ion with a relatively large size (and low hydration energy) will adhere less strongly to the water molecules than the ion with a smaller size (and relatively higher hydration energy). This suggests that an ion with a large size will easily interact with substrates than those with small size (Okiemen *et al.*, 1991).

3.3 Effect of temperature

The effect of temperature on the adsorption of Cu²⁺, As³⁺ and Cd²⁺ from solution by eggshell was studied at a concentration of 10mg/l for 180mins. Table 3

shows that the removal of Cu²⁺, As³⁺ and Cd²⁺ from aqueous solution by eggshell is temperature-dependent. Increase in temperature from 30°C to 60°C was found to result in a steady decrease in the removal efficiency of the adsorbent for the three metal ions. This is probably due to the effect of temperature on the interaction between the eggshell surface and the metal ions in solution.

Table 2: Initial concentration of ions in solution (c_i), concentration of metal ions in solution after sorption (c_t) and concentration of metals adsorbed at various concentrations (Y_t) at 30°C

C _i (mg/l)	c _i (mg/l)			Y _t (mg/l)		
	Cu ²⁺	Cd ²⁺	As ³⁺	Cu ²⁺	Cd ²⁺	As ³⁺
10	1.35	4.00	2.78	8.65	6.00	7.22
20	2.36	7.70	5.42	17.64	12.30	14.58
30	2.60	11.12	7.83	27.40	18.88	22.17
60	3.28	20.72	14.54	56.72	39.28	45.46
80	3.80	27.20	19.03	76.20	52.80	60.97

Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the eggshell thereby resulting in a decrease in the amount of metal ions adsorbed on the eggshell. This implies that the bond between the metal ions and the eggshell surface is a weak bond suggesting physical adsorption of the metal ions on the eggshell. Since the adsorption site of the ions on the eggshell surface is probably through the oxygen atoms of the carbonate group, increase in temperature also probably stretches the bond between these atoms and distorts the adsorption of the ions on the eggshell surface as also reported by Horsfall and Spiff (2005a).

The partition coefficient values obtained for 10mg/l each of the metal ions at different temperatures are shown in Table 3. Figure 4 shows the variation of partition coefficient of the metal ions with temperature. It could be seen from the figure that partition coefficient decreases as temperature is increased. The amount of metal ions adsorbed decreased as the temperature was increased from 30°C to 60°C. Figure 5 shows the Arrhenius plot for the adsorption of Cu²⁺, Cd²⁺ and As³⁺

by eggshell using the Arrhenius equation given in equation 3;

$$\log Y_t = \log A - \frac{E_a}{2.303RT} \dots\dots\dots 3$$

where Y_t is the amount adsorbed at temperature t, A is the Arrhenius constant, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. From the equation, a plot of log Y_t against 1/T gave a straight line from which E_a and A were obtained from the slope and intercepts, respectively. The low activation energy values of 8.50KJmol⁻¹, 9.25KJmol⁻¹ and 11.74KJmol⁻¹ obtained for the adsorption of Cu²⁺, As³⁺ and Cd²⁺ respectively suggest a physical adsorption mechanism. Table 4 gives the resulting values of E_a and log A derived from the slope and intercept, respectively.

3.4 Freundlich adsorption isotherm

Adsorption isotherms attempt to interpret the processes by which metal ions are bound to cellulosic materials and the stoichiometry of the metal ion-adsorbent interface after adsorption. In this study, Freundlich isotherm equation given in equation 4 was tested with the data generated because it is most applicable for adsorption from solution (Sharma and Sharma, 1999). It describes multi-layer adsorption in which the concentration of substance adsorbed does not depend on the existing concentration on the adsorbent surface but more on physical-based interaction with the adsorbent.

$$\frac{x}{m} = Kc^n \dots\dots\dots 4$$

The linearized form of this equation gives:

$$\log \frac{x}{m} = \log K + n \log c \dots\dots\dots 5$$

where $\frac{x}{m}$ is the concentration of metal ion adsorbed per unit mass of adsorbent (x is the amount of metal ion absorbed, m is the mass of adsorbent), c is concentration of metal ion in solution, K and n are empirical constants.

Table 3: Partition coefficients and removal efficiencies for Cu²⁺, As³⁺ and Cd²⁺ from aqueous solution at different temperatures

Temperature (°C)	Partition coefficient			Removal efficiency (%)		
	Cu ²⁺	As ³⁺	Cd ²⁺	Cu ²⁺	As ³⁺	Cd ²⁺
30	6.41	2.60	1.50	86.50	72.20	60.00
40	5.62	2.08	1.00	84.90	67.50	50.00
50	2.39	1.42	0.89	70.50	58.70	47.20
60	1.89	1.09	0.62	65.40	52.20	38.20

Table 4: Activation energy, Arrhenius constants and Freundlich isotherms for the adsorption of metal ions from 10 mg/l solution by eggshell

Metal ions	E _a (kJmol ⁻¹)	Log A	K	N	R ²
Cu ²⁺	8.50	2.281	0.186	0.952	0.999
As ³⁺	9.25	2.315	0.128	0.971	0.999
Cd ²⁺	11.74	2.614	0.036	0.957	0.999

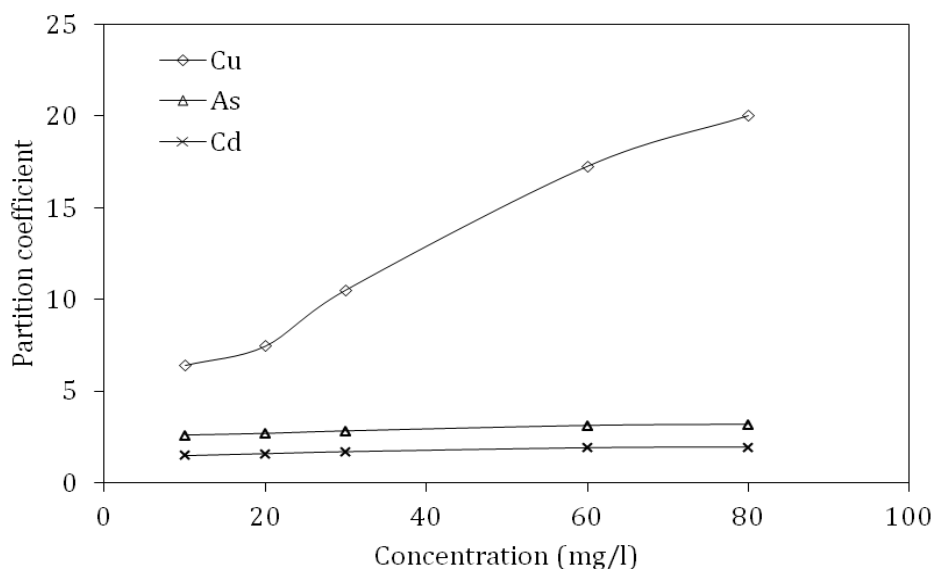


FIG. 3: Variation of partition coefficient of metal ions with initial concentration of metal ions in solution.

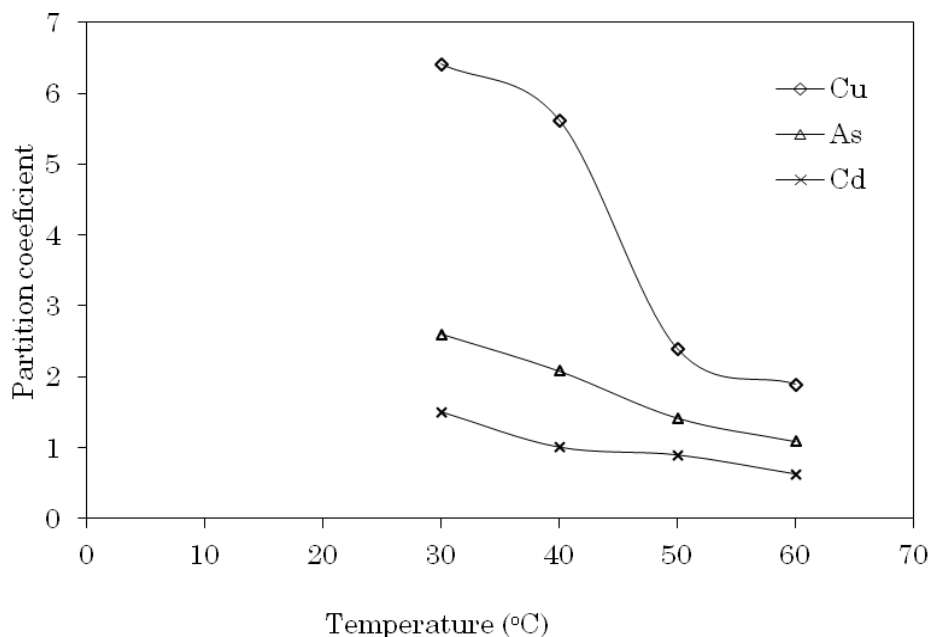


FIG. 4: Variation of partition coefficient with temperature.

It was found that the experimental data obtained for the adsorption of Cu²⁺, As³⁺ and Cd²⁺ from solution at 30°C within the concentration range of 10 – 80 mg/l fit the Freundlich adsorption isotherm as shown in figure 6.

The isotherm equation constants presented in Table 4 shows that the values of *n* are less than unity which is the nature (implying same order of magnitude) of *n*-values reported by Horsfall and Spiff (2005a, b). It is also reported by these authors that the more the *n*-value approaches unity, the closer the sorption process can be

represented by the Freundlich isotherm model. For the three metal ions under study, the *n*-values are consistent with Freundlich isotherm behaviour and data reliability (*R*²) was above 99% in all cases. Similarly, the more the *K*-value approaches unity, the higher the adsorption.

3.5 Kinetic modeling of sorption of metal ions from solution

In order to investigate the kinetics and mechanism of sorption of Cu²⁺, As³⁺ and Cd²⁺ by

eggshell and the potential rate-controlling steps, the different models used were pseudo-first order and pseudo second order kinetic equations. The study of

sorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time of adsorbate at the solid-liquid interface.

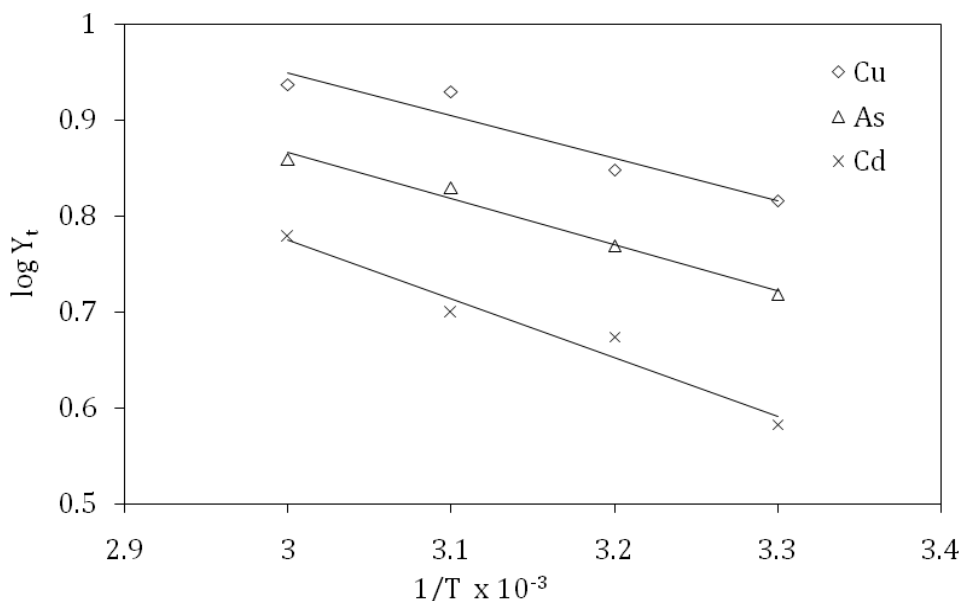


FIG. 5: Arrhenius plot for the adsorption of metal ions by eggshell.

The pseudo first-order equation is generally expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots\dots\dots 6$$

where q_e is sorption capacities at equilibrium, q_t is sorption capacities at time t and k_1 is rate constant of pseudo-first order sorption (Augustine *et al.*, 2007).

The linear form of equation 6 gives:

$$\log(q_e - q_t) = \log q_e - k_1 t \dots\dots\dots 7$$

A plot of $\log(q_e - q_t)$ against t gave a linear relationship as represented in figure 7 from which k_1 and q_e were determined from the slope and intercept of the plot respectively.

The pseudo second-order chemisorptions kinetic equation is generally expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \dots\dots\dots 8$$

where the terms remain same as in pseudo first-order, k_2 being the rate constant for the pseudo second order sorption ($\text{g.mg}^{-1} \cdot \text{min}^{-1}$). (Augustine *et al.*, 2007). Equation 8 has a linear form:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots 9$$

Let h (mg.g⁻¹.min⁻¹) which is the initial sorption rate as $q/t \rightarrow 0$ be given as:

$$h = k_2 q_e^2 \dots\dots\dots 10$$

Furthermore, equation 10 can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \dots\dots\dots 11$$

Applying the pseudo second-order kinetics to the experimental data, a plot of t/q_t versus t gave a linear relationship from which, q_e and h were determined from the slope and intercept of the plot, respectively. K_2 was derived by substituting q_e and h values into equation 10. Table 5 shows the experimental values of k_2 , q_e and h .

For an appropriate description of the mechanism of Cu²⁺, As³⁺ and Cd²⁺ sorption, it was necessary to test the different kinetic models to determine their extent of fitness to the experimental sorption data. The optimization procedure to select the best fit model requires the selection of an error function in order to evaluate the fit of the kinetic models to the experimental sorption data. The coefficient of determination, R^2 , was chosen as the error function for the kinetic model analysis. This is because linear regression implicitly minimizes the sum of the squares of

the errors to determine the parameters in the equation (Ho *et al.*, 2002).

Table 6 presents the R^2 values of the different kinetic models used to access the rate of sorption of the metal ions onto the eggshell adsorbent. Examination of Table 6 shows that the pseudo-second order kinetic equation had the highest R^2 values for Cu²⁺ while the pseudo-first order kinetic equation had the highest R^2 values for As³⁺ and Cd²⁺. Thus, pseudo-second order kinetic model was taken as the best fit model for the description of the mechanism of sorption of Cu²⁺ ions while pseudo-first kinetic model was taken as the best fit for the description of As³⁺ and Cd²⁺ ions. Similar conclusion was also reported for the sorption of some heavy metal ions onto various adsorbent surfaces (Benguella and Ben, 2002; Ho *et al.*, 2002).

Table 5: Kinetic constants for pseudo-second order equation

Metal ions	k_2 (g.mg ⁻¹ .min ⁻¹)	q_e (mg.g ⁻¹)	h (mg.g ⁻¹ .min ⁻¹)
Cu ²⁺	0.041	3.836	0.603
As ³⁺	0.048	6.173	1.829
Cd ²⁺	0.058	8.886	4.580

Table 6: Linear coefficient of determination (R^2) of kinetic models

Kinetic models	R^2 values		
	Cu ²⁺	As ³⁺	Cd ²⁺
Pseudo-first order	0.889	0.835	0.753
Pseudo-second order	0.929	0.736	0.496

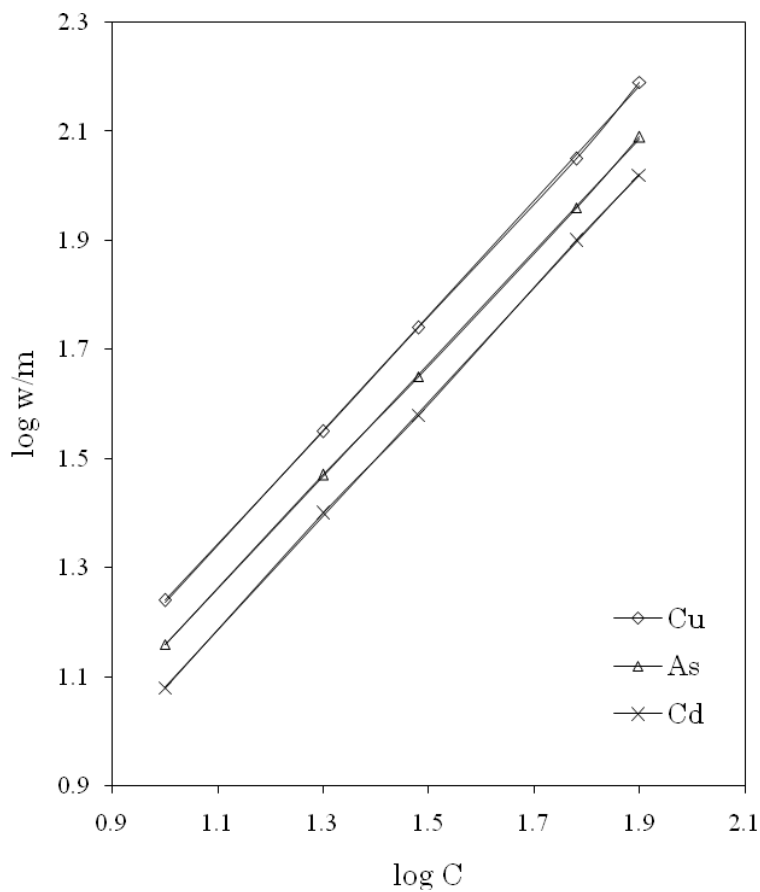


FIG. 6: Freundlich adsorption isotherm for the adsorption of metal ions from solution by eggshell.

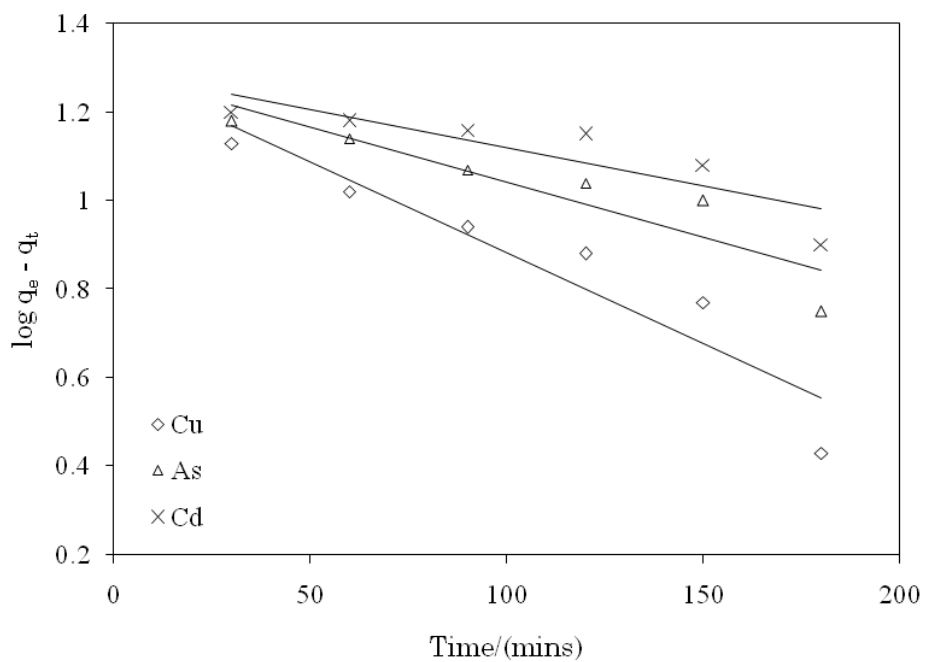
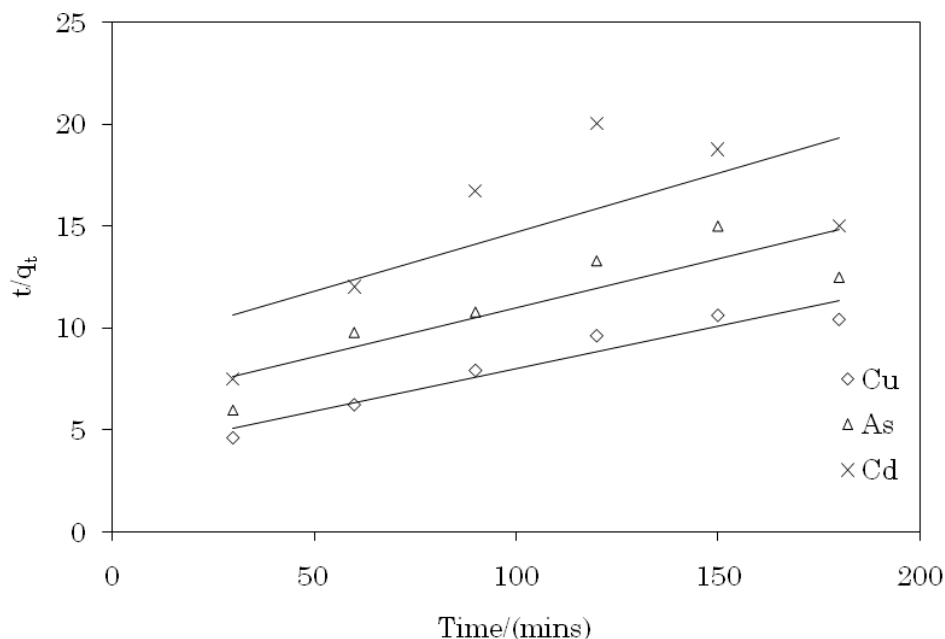


FIG. 7: Variation of $\log (q_e - q_t)$ with contact time.


 FIG. 8: Variation of t/q_t with contact time.

CONCLUSIONS

The aim of this study was to investigate the sorption capacity of chicken eggshell for Cu^{2+} , As^{3+} and Cd^{2+} from aqueous solutions based on the effect of contact time, initial metal ion concentration in aqueous solution and temperature. The partition coefficient, and likewise, the sorption capacity of chicken eggshell increases with increase in contact time and concentration of metal ion in solution but decreases with increase in temperature. The force of attraction between the metal ions and eggshell is weak which is indicative of physical adsorption as supported by the low activation energies obtained for the metal ions.

It therefore suffices to conclude that chicken eggshell could serve as a cheap, readily available and effective adsorbent for the removal of Cu^{2+} , As^{3+} and Cd^{2+} from wastewater as a way of treatment before discharge into the environment.

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